

COATINGS

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HIGH-TEMPERATURE COATINGS FOR HEAT-INSULATING FIBER MATERIALS

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Functional coatings for heat-shielding and heat-insulating materials based on quartz fibers and filamentary crystals are examined.

Key words: coating, erosion resistance, firing, heat flux, radiant energy, absorption, reflection, silicon nitride, heat resistance.

During orbital flights in near-Earth space the surface of the spacecraft is exposed to the entire solar radiation spectrum from UV to IR. Most of the transmitted thermal energy is in the infrared part of the solar spectrum [1].

The emission and absorption of solar energy occur simultaneously and independently of one another, i.e., all bodies can emit and absorb the electromagnetic radiation incident on them.

The temperature of the outer surface of the spacecraft can be determined approximately from the heat balance equation

$$q_r = q_e \quad \text{or} \quad \alpha_s S = \varepsilon \sigma T^4,$$

where q_r and q_e are the specific heat flux of radiant energy absorbed and emitted by the body, respectively; α_s is the total hemispherical absorption coefficient for solar radiation; S is the specific heat flux of solar radiation at the boundary of the Earth's atmosphere in a direction normal to the irradiated surface; ε is the total hemispherical emissivity; σ is the Stefan–Boltzman constant; and, T is the surface temperature of the spacecraft, K:

$$T = \sqrt[4]{\frac{S}{\sigma} \frac{\alpha_s}{\varepsilon}}.$$

Substituting the values of S and σ we obtain

$$T = 395 \sqrt[4]{\frac{\alpha_s}{\varepsilon}}.$$

It follows from this relation that the main parameter determining the surface temperature of the spacecraft in orbital flights is the ratio of the absorption to the emission coefficient. We note that if the value of α_s corresponds to spectrum of the solar rays, the value of ε corresponds to the infrared rays at a given temperature of the wall.

According to the technical specifications the ratio α_s/ε must be 0.4. Therefore the initial components must have definite optical characteristics.

Data on the system of “white” ceramic coatings for heat-shielding tiles are available. A coating consists of an optically regulated sublayer and a protective outer coating and has a high emissivity and low ratio $\alpha_s/\varepsilon = 0.35$. The introduction of aluminum oxide into a SiC – quartz-glass coating lowers the absorption coefficient α_s for solar radiation from 0.5 to 0.3 with no significant effect on the emissivity. Titanium dioxide additions decrease α_s further. Zinc oxide and zinc orthotitanate are used as pigments with low absorptance. It has been reported that coatings based on silicon dioxide with boron anhydride additions have been used. Aluminum oxide is introduced to improve reflectance.

The characteristics of the substrate to be coated must be taken into account when choosing material with high reflectance. To ensure heat-resistance the coating's CLTE must be close to that of the substrate.

For materials based on amorphous silicon dioxide it is important that the amorphous state is preserved, because crystallization with formation of α -cristobalite changes the volume significantly and as a result the material breaks down. Most additives, boron oxide being an exception, make quartz glass more prone toward crystallization; oxides of alkali and alkaline-earth metals are especially dangerous.

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In this connection quartz glass (silicon dioxide content 99.9 wt.%) and high-silica glass can serve as the basis for creating high-reflectance coatings.

According to the reference data the total visible-range absorption coefficient for quartz glass equals 0.05–0.2, while the total emissivity equals 0.93 at temperature 20–500°C. Hence it follows that quartz glass satisfies the requirements imposed on materials to be used for high-reflectance coatings. High-silica glasses also meet these requirements.

The studies were performed on 50 × 50 × 46 mm samples and 150 × 150 × 46 mm tiles made from TZMK-10.

The following were used in this work: quartz glass with > 99.96% SiO₂; TSM-514 high-silica glass; LK-5 borosilicate glass; and, S-14 and TSM-548 high-silica glasses.

The moisture barrier properties of the coating were determined by the drop-liquid method as well as by immersing the coated tile into distilled water according to the water absorption:

$$W = \frac{P_1 - P_0}{P_0},$$

where W is the water absorption, %; P_0 is the mass of the coated tile before immersion into water; and, P_1 is the mass of the coated tile after being kept in water for a definite period of time.

The heat-resistance of the coating was determined by the VIAM method in the regime 20–800°C and at the Central Aerohydrodynamic Institute in the regime –130–800°C. The density of the coating was found by well-known procedures, and the specific surface area was found using the PSKh-4 apparatus.

X-ray phase analysis for the content of α -cristobalite was performed by the x-ray diffraction method with a DRON-3 diffractometer. The reflectance α_s for solar radiation was determined with an FM-85 photometer. The coating thicknesses were found by a destructive method: the coating was cut off the sample, fiber was removed from the coating and the thickness was measured with an MBS-2 binocular microscope with an eyepiece micrometer.

The shrinkage of the tiles made from the TZMK-10 material was determined by the VIAM method: the change in the linear dimensions of the tiles was measured before and after firing of the coating and tests at high temperatures. The shrinkage of the samples was calculated using the relation $Sh = A_1 - A_0$, where A_0 and A_1 are, respectively, the dimensions of the coated plate before and after the plate is heat-treated.

The linear dimensions were measured with a slide caliper to within 0.05 mm and by the indicator method to within 0.01 mm.

The erosion resistance of the coating in a gas stream was determined by placing the samples into the gas efflux zone of the combustion chamber of a liquid-fuel rocket motor. The

test conditions were: gas temperature 800°C, duration 20 min and stream pressure 0.1 MPa.

The resistance to UV radiation was determined by the VIAM method. The climatic tests were performed in a humidity chamber with $\phi = 98\%$ and temperature 50°C and in a tropical climate chamber following OST1 90242–76; the resistance to radiation was determined according to OST1 90242–76. The dielectric properties of the coating were determined according to GOST 89215–72. The ultimate tensile strength was found in accordance with the VIAM standard.

In choosing materials for creating high-reflectance coatings the particulars of the substrate to be used with the coating must be taken into account [2].

Quartz and high-silica glasses can serve as a base for the erosion-resistant coatings for TZMK-10 type material. The composition of TSM-514 high-silica glass with the following composition was studied (wt.%): 94–96% SiO₂, 3.5–6% B₂O₃ and other — aluminum and sodium oxides.

In the course of the work with the coating, analysis of the statistical data revealed instability of the coating's moisture-barrier characteristics. This is due to the difference of the content of the main components in the high-silica TSM-514 glass. When the silicon oxide content was increased from 93 to 95% and the boron anhydride content from 4–5 to 1% it was impossible to obtain a moisture barrier coating.

The main direction of synthesis became the creation of a coating based on high-silica glasses with a stable composition as well as thermal and physical properties in a wide temperature – time interval.

The possibility of obtaining a coating based on S-14 glass and compositions from TSM-514 high-silica glass + S-14 glass was investigated. The drawbacks of coatings based on S-14 glass include a high CLTE and the glass's proneness toward the formation of α -cristobalite during firing. As a result cracks are observed to form in the coating after firing.

The advantages of TSM-548 glass include: stability of the chemical composition (small variance with respect to the main components), low content of alkali oxides (to 0.37%) and low CLTE — $\alpha = 1 \times 10^{-6} \text{ K}^{-1}$.

An advantage of the coating based on TSM-548 high-silica glass is that its firing temperature is lower compared with other compositions.

The coating compositions developed have passed experimental and industrial tests. The coatings were tested on tiles made from TZMK-10 material with different heights ranging from 46 to 20 mm and smaller. There is virtually no deformation on 30 mm high tiles with coating based on TSM-548 high-silica glass. The use of a coating based on TSM-548 high-silica glass made it possible to increase the good yield from 40 to 70% and after perfecting the coating preparation and deposition technology to > 90%.

A wide complex of properties of coatings based on TSM-548 high-silica glass was investigated (Table 1).

TABLE 1. Properties of ÉVS-4 Coating Based on TSM-548 High-Silica Glass

Indicator	According to TS*	ÉVS-4 coating
Working temperature, °C	From –130 to +800	From –130 to +800
Coating density, g/cm ³	> 2.2	1.8 ± 0.1
Thickness range, mm	0.3 ± 0.1	0.3 ± 0.1
Heat-resistance in the regime 20 ⇌ 800°C, cycle	105	105
α_s/ε ratio	≤ 0.4	0.18
CLTE, 10 ^{–6} · K ^{–1}	–	0.8 – 1.2

* TS) technical specification.

TABLE 2. Properties of Silicon Nitride

Material	Density, g/cm ³	Ultimate tensile strength, MPa	Modulus of elasticity, GPa	CLTE, 10 ^{–6} · K ^{–1}
Powder	3.19	–	460 – 480	2.75
Filamentary crystals	3.19	30 – 35	3800 – 5100	2.5 – 3.5

These studies led to the development of a white erosion-resistant water-resistant coating for TZMK-10 material that meets the technical specifications. This coating was given the designation ÉVS-4.

The characteristics of the ÉVS-4 coating were determined: absorption coefficient for solar radiation $\alpha_s = 0.14$ – 0.17 and the ratio $\alpha_s/\varepsilon = 0.18$; thermal resistance, corrosion resistance, ultimate tensile strength, modulus of elasticity, funginertness, resistance radiation, dielectric constant $\varepsilon = 1.24$, tangent of the angle of dielectric losses $\tan \delta = 0.011$ at $f = 10$ Hz. Climate tests were performed on the coating [3].

Light-weight, non-metallic, heat-shielding materials based on ceramic fibers occupy a special place among composite materials. They possess a complex of valuable properties: low density, high thermal conductivity and high thermal stability. Examples are materials based on silicon nitride Si_3N_4 filamentary crystals.

At present silicon nitride is increasingly finding applications for obtaining fireproof articles and in composite ceramic materials because of its refractory nature and quite high resistance [4, 5]. However, oxygen oxidizes 14.71% of Si_3N_4 powder in 3 h at high temperatures of the order of 1000°C and 23.6% at 1300°C. In air oxidation starts at 1000°C — the degree of decomposition is 0.11%, increasing to 0.2 – 0.3% per 100°C to 1400°C. In air silicon nitride oxidizes with SiO_2 being formed and N_2 released. When heated in vacuum in the temperature interval 800 – 1200°C silicon nitride dissociates into Si and N_2 .

Under certain conditions silicon nitride can be obtained in the form of filamentary crystals, whose properties differ somewhat from powdered material (Table 2).

It is evident from the data in Table 2 that filamentary Si_3N_4 crystals possess high tensile strength and a higher modulus of elasticity than powdered material. In addition, filamentary Si_3N_4 crystals are more resistant to oxidation at high temperatures. This combination of properties makes it possible to use them for creating light-weight heat-shielding materials.

The VTNK-brand heat-shielding material based on filamentary Si_3N_4 crystals was created at VIAM using amorphous silicon dioxide as the binder.

Properties of VTNK-Brand Material

Density, g/cm ³	0.15
Thermal conductivity, W/(m · K), at temperature:	
100°C	0.09
800°C	0.05
Ultimate compression strength, MPa	3.7 – 5.8
Modulus of elasticity in compression	240

Together with the complex of valuable properties low erosion resistance in gas flows and high water absorption are characteristic for highly porous, heat-shielding materials. This makes it necessary to develop protective coatings.

The ÉVCh-5 brand erosion-resistant moisture-barrier coating was developed for the VTNK heat-shielding material for use in the temperature range 1300 – 1400°C.

It was determined that with prolonged firing of a coating in air at high temperatures an exothermal oxidation reaction of Si_3N_4 develops in the VTNK material, which results in burn-through of the samples. In this connection the admissible temperature – time regimes for coating formation on samples of the VTNK material in air were determined: at 1000°C the soaking time is unlimited; at 1200°C no appreciable changes occur in the material with soaking times to 7 min.

X-ray phase analysis showed that a very small amount of silicon tetraboride is present in the interior of the coating; almost all of the silicon tetraboride in the surface layer oxidizes during firing.

The effect of the chemical composition of the coatings on their moisture barrier properties in admissible temperature – time formation regimes was investigated. In these regimes moisture-barrier coatings were obtained on the basis of high-silica and borosilicate glasses and silicon tetraboride.

It was determined that to prepare ÉVCh-5 coatings it is necessary to use high-silica and borosilicate glass powders with the content of particles with diameter to 10 μm — 45 wt.% and 30 – 40 μm — 5 wt.%. The conditions of slip feeding from paint sprayer onto the sample have the greatest effect on the formation of the coating layer during spraying. A moisture barrier coating is obtained by spraying slip at the rate 2 cm³/sec. The higher the value of this parameter the looser the coating layer obtained is.

The emissivity of the coating in the interval 350 – 1400°C is higher than 0.87.

The following tests were performed on the coating:

- resistance to cyclic changes in temperature and pressure; no damage to the coating was observed after 10 test cycles with maximum temperature 1300°C;
- erosion resistance in air plasma with surface temperature 1350°C;
- temperature stability in vacuum at residual pressure 133.3×10^{-3} MPa and temperature 1300°C.

It was determined that the coating possesses satisfactory erosion resistance and temperature stability in vacuum.

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